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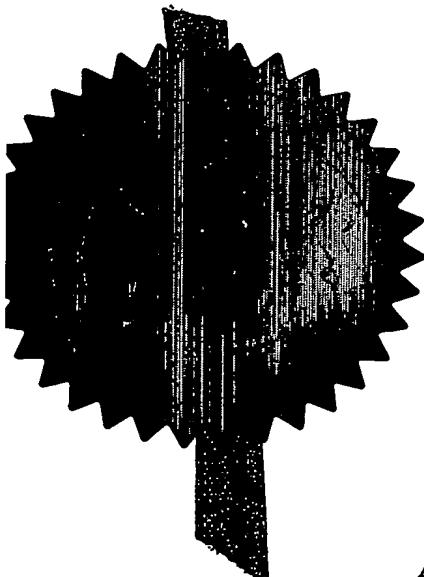
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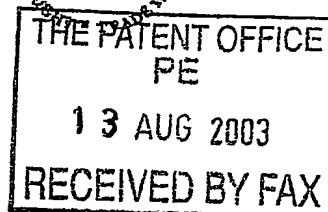
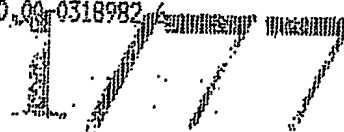
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JOHNSON MATTHEY PUBLIC LIMITED COMPANY
2-4 COCKSPUR STREET
TRAFALGAR SQUARE
LONDON SW1 5BQ

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

GB

536262007

4. Title of the invention

METHOD OF DECOMPOSING NITROGEN DIOXIDE

5. Name of your agent (if you have one)

ANDREW DOMINIC NUNN

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

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0308944.8

17 April 2003

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DECOMPOSING INTERNAL COMBUSTION ENGINE EXHAUST NO₂

relates to a method of decomposing nitrogen dioxide (NO₂) in a exhaust gas mixture of an internal combustion engine.

Internal combustion engines emit a mixture of pollutants (CO, unburned hydrocarbons (HC), nitrogen oxides (NO_x) and NO_x component can decompose into nitrogen monoxide (NO) and level of these pollutants in exhaust gases from internal combustion engine to atmosphere is regulated by legislation. Such legislation engine management, exhaust gas aftertreatment, and other measures.

One method primarily for treating exhaust gas comprises an oxidation catalyst converting exhaust gas to NO₂ and a particulate filter for trapping PM. A method that uses this arrangement is described in EP 03 41382 or US 6,340,000 which are incorporated herein by reference. The process comprises a diesel exhaust gas, containing PM and NO, is filtered over an oxidation catalyst converting NO to NO₂, collecting PM on the filter and regenerating the filter by oxidizing the NO₂. This technology is commercially available as Johnson High Efficiency Particulate Trapping or CRT®. Oxidation of the PM in the NO₂ results in a reaction leading to the complete reduction of the NO₂ to N₂ as

One process is that it is possible to decompose diesel soot at temperatures of about 500°C and above. Oxidation of diesel soot in oxygen occurs at about 500°C and above. Exhaust gas is generally at a temperature of about 500°C and above. Exhaust gas from gasoline engines is generally at a temperature of about 500°C and above. Problems arise in the system if the temperature is too low for the oxidation of soot in oxygen without the provision of additional means for raising the temperature; so-called "cold start" problems arise in these regimes.

The process described in EP 03 41382 is that, as exhaust emission limits become more stringent, legislative bodies have begun to regulate NO₂ it is permissible to decompose NO₂ in the exhaust gas before it is released to the atmosphere. For example,

the California Air Resources Board (CARB) has proposed that a maximum of 20% of tailpipe NO_x of the relevant drive cycle is emitted as NO_2 . NO_2 is toxic and can cause headaches, dizziness and nausea in low doses. It also has an objectionable smell. If there is insufficient PM on the filter to react with NO_2 generated over the oxidation catalyst or the temperature of the exhaust gas is below a preferred range for combustion of PM in NO_2 , NO_2 can slip past the filter and be undesirably exhausted to atmosphere.

This problem is particularly acute when internal combustion engines are used in confined spaces, such as mines, where vehicles are used to drill for, load, and transport mined material to the surface. Many mining operations generate particulate matter, and so exhaust aftertreatment systems comprising filters for reducing the levels of PM emitted are being considered. Furthermore, explosives used to blast rock to recover a desired ore can generate NO_2 . Accordingly, it would be an advantage to reduce the exhaust gas emissions of both PM and NO_2 to the atmosphere in closed environments to improve the health and safety of miners. Indeed, the US Mine Safety and Health Administration prevents the use of diesel exhaust systems comprising diesel particulate filter systems that increase NO_2 emissions.

In selective catalytic reduction (SCR) by hydrocarbons (HC), HC react with NO_x , rather than with O_2 , to form nitrogen, CO_2 and water according to equation (1):



The competitive, non-selective reaction with oxygen is given by Equation (2):



Two preferred groups of HC-SCR catalysts to selectively promote the desired reaction (1) for catalysing HC-SCR of NO_x (HC-SCR catalysts are also referred to as "lean NO_x catalysts" (LNC), "De NO_x catalysts", " NO_x occluding catalysts", " NO_x reducing catalysts" and even "non-selective catalytic reduction catalysts" (because they can catalyse non-selective reactions e.g. Equation (2)). These two preferred groups are platinum on alumina and copper-substituted zeolite such as Cu/ZSM-5.

Pt-based catalysts tend to operate at relatively low temperature (peak activity $\sim 250^{\circ}\text{C}$) and have a relatively narrow temperature window for HC-SCR activity whereas zeolite-based HC-SCR catalysts have a wider temperature window than Pt-based HC-SCR catalysts and operate at higher temperatures (peak activity $\sim 400^{\circ}\text{C}$).

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One potential solution to this problem is described in EP 0758713, where in one embodiment, an exhaust system comprises an optionally platinum-based oxidation catalyst and a diesel particulate filter (DPF) in the CRT[®] configuration and a NO_x absorbent downstream of the DPF. The NO_x absorbent can comprise platinum for oxidising NO to NO₂ in $\lambda > 1$ exhaust gas compositions, rhodium for reducing NO_x to N₂ in $\lambda < 1$ exhaust gas compositions and at least one substance selected from alkali metals such as potassium and caesium; alkali-earth metals such as barium and calcium; and rare-earth metals such as lanthanum for absorbing the NO₂ and storing it as the nitrate. Catalyst compositions comprising platinum, rhodium and a NO_x absorbent material are typically called NO_x traps.

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In a second embodiment, a NO_x reducing catalyst is disposed downstream of the filter for catalysing the reduction of the NO_x to N₂ using diesel HC fuel and CO. The NO_x reducing catalyst can be a zeolite such as ZSM-5 ion exchanged with copper or iron, or mordenite supporting platinum. However, it is clear from EP 0758713 that HC reductant for reducing the NO_x is introduced into the exhaust system either by injecting additional fuel during the exhaust cycle or directly into the exhaust passage. In either case, injection is done always upstream of the CRT[®] oxidation catalyst.

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In our WO 03/037507, we describe an exhaust system for an internal combustion engine comprising a catalyst, such as a platinum-based catalyst, for oxidising NO to NO₂ when the exhaust gas composition is $\lambda > 1$; and a filter disposed downstream of the NO oxidation catalyst, i.e. in the CRT[®] configuration. The filter can comprise an oxidation catalyst such as platinum and/or palladium, rhodium and a NO_x absorbent material, such as any of those described in EP 0758713 above. The filter component *per se* of this arrangement is described in Japanese patent no. 2722987.

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We have investigated ways of catalytically decomposing NO₂ to NO and we have found that, very surprisingly, certain known HC-SCR catalysts are particularly active. In order to optimise conversion, we found that a small amount of HC reductant is desirable. However,

whilst our results show that a small amount of reduction to N_2 is effected, very good NO_2 conversion to NO can be achieved. It will be noted that for HC-SCR, HC: NO_x ratios of from between 2 to 6 are preferred in the above-mentioned temperature windows. Our results show that NO_2 decomposition can be effected at much lower temperatures and HC: NO_x ratios.

According to a first aspect, the invention provides a method of decomposing nitrogen dioxide (NO_2) in an exhaust gas of a lean-burn internal combustion engine, which method comprising adjusting the HC: NO_x ratio of the exhaust gas to from 0.1 to 2 and contacting this gas mixture with at least one support comprising at least one metal selected from the group consisting of rhodium, silver, iron and copper.

NO_2 can account for up to about 50% NO_x in the exhaust gas of an internal combustion engine. Therefore, according to one embodiment the HC: NO_2 ratio is adjusted to from 0.05 to 1.

We have found that for the prescribed HC: NO_x ratios, NO_2 conversion is reduced at lower temperatures. In order to meet the proposed CARB threshold of a maximum of 20% NO_2 of NO_x emitted, in one embodiment we prefer that the step of adjusting the HC: NO_x ratio is performed only when the exhaust gas temperature is at 250°C and above. It will be noted that NO_2 conversion is possible at temperatures much below that required for HC-SCR for a similar catalyst i.e. above 250°C for NO_2 conversion vs. about 400°C for HC-SCR over Fe-Beta zeolite.

According to a further embodiment, the step of adjusting the HC: NO_x ratio is done when the exhaust gas temperature is in a range that has been pre-determined to produce increased NO_2 in the exhaust system. Such temperature range will usually depend on the engine type and the duty of the vehicle. Illustrative embodiments include city centre buses comprising heavy duty diesel engines (250 - 300°C); buses in non-city centre locations (up to 400°C); and heavy duty diesel trucks (up to 500°C).

Potentially, the method according to the first aspect of the invention can be used to treat gas mixtures including NO_2 generated by any chemical, e.g. industrial, process. However, for the purposes of the present invention, the method is for treating an exhaust gas mixture derived from combustion of a hydrocarbon fuel, such as diesel fuel, gasoline fuel, natural gas (NG) or liquid petroleum gas (LPG) in an internal combustion engine.

According to a second aspect, the invention provides an exhaust system for an internal combustion engine, which system comprising a catalyst for decomposing NO_2 with a suitable reductant, and means, in use, for adjusting the $\text{HC}:\text{NO}_x$ ratio in an exhaust gas upstream of the catalyst to from 0.1 to 2, which catalyst comprising at least one support comprising at least one metal selected from the group consisting of rhodium, silver, iron and copper.

In one embodiment, the means for adjusting is adapted to adjust the $\text{HC}:\text{NO}_2$ ratio of the exhaust gas to from 0.05 to 1.

According to a further embodiment, the adjustment means is controlled, in use, to operate when the exhaust gas temperature is above 250°C .

In another embodiment, the adjustment means is controlled, in use, to operate when the exhaust gas temperature is below 500°C .

Control of the adjustment means can be effected by suitable means comprising, in one embodiment, a processor which in turn can form part of the engine control unit (ECU) if desired.

In order to control the $\text{HC}:\text{NO}_x$ ratio, it is desirable that the system comprises one or more sensors for inputting the status of one or more of the following conditions in the system: exhaust gas temperature; catalyst bed temperature; exhaust gas mass flow; NO_2 in the exhaust gas, e.g. as detected by a suitable NO_2 sensor; manifold vacuum; ignition timing; engine speed; throttle position; lambda value of the exhaust gas composition; quantity of fuel injected in the engine; position of an exhaust gas circulation valve; and boost pressure.

It will be understood that the $\text{HC}:\text{NO}_x$ ratio can be varied according to the or each input received. For example, at lower exhaust gas temperatures a higher ratio is desirable for a pre-determined NO_2 conversion, whereas a lower $\text{HC}:\text{NO}_2$ ratio can be used at higher temperatures.

According to another embodiment, the control means is operated according to stored look-up tables or an engine map in response to at least one of the above inputs.

Adjustment of the $\text{HC}:\text{NO}_x$ ratio to within the prescribed range can be done either by increasing the amount of HC or by adjusting the NO_x e.g. by adjusting the amount of exhaust gas

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According to a further embodiment, the oxidation catalyst is associated with a NO_x absorbent material. One such arrangement is that the NO_x absorbent material, typically at least one compound of an alkali metal e.g. potassium or caesium, at least one compound of an alkaline earth metal, such as barium, strontium or calcium, or at least one compound of a rare earth metal, for example lanthanum or yttrium, is associated with the oxidation catalyst. Generally, the compounds will be oxides but, in use, the compounds may also be present as hydroxides, carbonates or, following NO_x absorption (as will be described hereinafter) nitrates.

In this arrangement, NO₂ generated over the oxidation catalyst during $\lambda > 1$ conditions can be absorbed in the NO_x absorbent material and stored as the nitrate. Since the NO_x absorbent material has a finite capacity to absorb NO_x, it is necessary periodically to regenerate it, i.e. to remove the stored NO_x. Generally, this is done in practice by transiently adjusting the λ composition of the exhaust gas to the rich side, i.e. $\lambda < 1$, for example by introducing additional HC fuel into the exhaust gas or by allowing less air into the combustion mixture. The nitrate forms of the alkali, alkaline earth and rare earth metals are understood to be unstable in rich exhaust gas, and so NO_x is released, in what is believed to be a mixture of at least NO and NO₂.

Typically, compositions comprising NO_x absorbent materials also comprise rhodium for reducing the NO_x to N₂ in the presence of the reductant. However, the rhodium NO₂ decomposition catalysts of the present invention do not include other PGM's such as platinum and/or palladium commonly used as oxidation catalysts. In one arrangement, for example, the NO₂ decomposition catalyst is on a separate monolith downstream of the filter. In a particular embodiment, however, the NO₂ decomposition catalyst can be disposed on a downstream end of the filter.

The filter can be any suitable substrate including a wall-flow filter of ceramic material such as silicon carbide or cordierite. Alternatively, it can be the device described in either EP 1057519 or WO 03/038248.

In one embodiment the at least one support for use in the NO₂ decomposition catalyst is selected from alumina, ceria, zirconia, titania, silica, chromia, a zeolite or a mixture, composite oxide or mixed oxide of any two or more thereof.

"Composite oxide" as defined herein means a largely amorphous oxide material comprising oxides of at least two elements which are not true mixed oxides consisting of the at least two elements.

5 In a further embodiment, the composite oxide or mixed oxide is selected from silica-alumina, a silica-zirconia, alumina-zirconia, alumina-chromia, alumina-ceria, ceria-titania or ceria-zirconia.

10 Examples of suitable zeolite components for the NO₂ decomposition catalysts are ZSM-5, β -zeolite, Y-zeolite or mordenite.

15 In each case, the support can be doped with at least one of lanthanum, barium, cerium, tungsten, silica and manganese to improve the stability of the support to high temperature ageing, act as a promoter in the decomposition of NO₂ and/or improve the oxygen storage capacity of the system, particularly in the case of manganese.

20 The NO₂ decomposition catalysts can be prepared according to known methods such as wet impregnation of the at least one support material using a suitable metal salt followed by calcination, or by ion exchange.

In one embodiment, the at least one support for use in the exhaust system according to the invention can comprise from 0.1 to 5.0 wt% rhodium, such as from 0.25 to 2.5 wt% rhodium, based on the total weight of the support.

25 In a specific embodiment, the catalyst comprises 0.5 wt% rhodium supported on alumina.

30 An important feature of the invention is that the support on which the rhodium is supported is devoid of other platinum group metals. Furthermore, the supported rhodium is not mixed with other support(s) supporting non-rhodium PGMs. Put another way, the supported rhodium is segregated from non-rhodium PGMs present in the exhaust system.

The method and exhaust system of the present invention are different from those described in EP 0758713 and PCT/GB02/004750 in that in the prior art, the rhodium is a component in a NO_x trap composition, i.e. it is associated with other catalysts such as platinum

and NO_x absorbent materials such as potassium, caesium and calcium. Furthermore, it is understood from the description of e.g. EP-A-1079084 discussed in PCT/GB02/004750 that any rhodium present would be on the upstream end of the filter.

5 In a further embodiment, the at least one support comprises from 1 to 10 wt% copper, such as from 2.5 to 7.5 wt% copper, based on the total weight of the support. Where the at least one support comprises a zeolite, it can be impregnated or ion exchanged onto the support.

10 In a further embodiment, the at least one support comprises from 1 to 10 wt% iron, such as from 2.5 to 7.5 wt% iron, based on the total weight of the support. Where the at least one support comprises a zeolite, it can be impregnated or ion exchanged onto the support.

In a specific embodiment the catalyst comprises 5 wt% iron and the at least one support is zeolite ZSM-5 and/or β -zeolite.

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According to a further embodiment, the at least one support comprises from 0.1 to 5.0 wt% silver, such as from 0.25 to 2.5 wt% silver, based on the total weight of the support.

20 In a specific embodiment, the catalyst comprises particulate ceria mixed with 2 wt% silver supported on alumina in a weight ratio of 1:4.

25 According to a third aspect, the invention provides an internal combustion engine comprising an exhaust system according to the invention. Such engine can be fuelled by any suitable fuel such as diesel fuel, gasoline fuel, natural gas (NG) or liquid petroleum gas (LPG).

According to a fourth aspect, the invention provides a vehicle, such as a mining vehicle, comprising an engine according to the third aspect of the invention.

30 It is believed that the NO₂ decomposition catalysts described herein, in addition to catalysing the reduction of NO₂, may also catalyse the reduction of SO₃ to SO₂ in exhaust gas conditions and can be used where such reaction is desirable, e.g. to reduce the amount of SO₃-derived particulate observed in diesel drive cycles.

In order that the invention may be more fully understood, the following Examples are provided by way of illustration only and with reference to the accompanying drawings, in which:

Figure 1 is a graph showing %NO₂ conversion as a function of temperature (°C) for NO₂ decomposition catalysts with and without diesel fuel injection (about 120ppm C1 (MK1)) relative to a blank reactor control; and

Figure 2 is a graph showing NO production from NO₂ in the presence of diesel fuel as a function of temperature relative to a blank reactor control;

Figure 3 is a graph showing NO₂ decomposition over a Cu/Beta-zeolite catalyst at HC:NO₂ of 0.5 as a function of temperature;

Figure 4 is a graph showing %NO₂ conversion over a Cu/Beta-zeolite catalyst at HC:NO₂ of 0.5 as a function of temperature;

Figure 5 is a graph showing NO₂ / NO_x ratio (%) over a Cu/Beta-zeolite catalyst at HC:NO₂ of 0.5 as a function of temperature;

Figure 6 is a graph showing NO₂ decomposition over a Cu/Beta-zeolite catalyst at HC:NO₂ of 0.25 as a function of temperature;

Figure 7 is a graph showing NO₂ / NO_x ratio (%) over a Cu/Beta-zeolite catalyst at HC:NO₂ of 0.25 as a function of temperature; and

Figure 8 is a graph showing NO₂ / NO_x ratio (%) over a Cu/Beta-zeolite catalyst at HC:NO₂ of 0.25 as a function of temperature.

Example 1

A series of catalysts were analysed on a simulated catalyst activity test (SCAT) gas rig for their abilities to decompose NO₂ in a simulated exhaust gas reaction mixture that contains 200ppm NO₂, about 120ppm C1 diesel fuel (MK1), 12% O₂, 4.5% CO₂, 4.5% H₂O and 20ppm SO₂, N₂ balance. Each catalyst was heated in a 10°C-a-minute ramp in the reaction mixture from

150°C to 500°C. The catalysts tested were 5 wt% ion exchanged ZSM-5 zeolite ((by total weight of the support) 5Cu/ZSM5), 0.5 wt% rhodium on alumina ((by total weight of the particulate support) 0.5Rh/Al₂O₃) and 5 wt% ion exchanged β -zeolite ((by total weight of the support) 5Cu/Beta).

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As a control, NO₂ decomposition over the blank reactor with mesh was measured and the 5Cu/ β -zeolite catalyst was tested with the above mixture but in the absence of diesel fuel. As a further test, the 5 wt% ion exchanged ZSM-5 zeolite was tested in the above exhaust gas reaction mixture wherein the 200ppm NO₂ was exchanged for 100ppm NO and 100ppm NO₂, i.e. 1:1 NO:NO₂. The results of NO₂ decomposition and NO production from NO₂ are set out in Figures 1 and 2.

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It can be seen that the addition of diesel improves the low temperature conversion of NO₂ to NO. The 5Cu/ β -zeolite catalyst is the most active catalyst giving 100% NO₂ removal from 200 to 350°C.

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Changing the gaseous NO_x composition from 200ppm NO₂ to 100ppm NO/100ppm NO₂ has no perceptible effect on the low temperature performance, although the activity does fall off more sharply at the high temperature end when using the NO/NO₂ mix. Whether this is due to NO inhibition (perhaps unlikely at this high temperature) or is a kinetic/reaction order effect associated with reducing the inlet NO₂ concentration from 200 to 100ppm is not yet clear.

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The mass balances for NO₂ decomposition vs. NO production at temperatures in the 300-400°C range do not correlate. For example, at 350°C the NO₂ removal is 100%, but only around 150ppm NO is seen in the gas phase (instead of the 200ppm which we would expect to see if all of the NO₂ was being decomposed to NO). We believe, therefore, that we are getting some lean NO_x reduction here, using stored HC and gas phase HC to remove the NO_x - the temperature window fits with this hypothesis.

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Example 2

In a laboratory, a bench mounted, heavy-duty diesel engine fitted with a CRT[®] exhaust gas after-treatment system as described in EP 0341832, i.e. a platinum on aluminium based oxidation catalyst for oxidising NO to NO₂ and a ceramic wall-flow diesel particulate filter, was

used to test the principle of NO_2 decomposition shown in Example 1 in "real-world" conditions. A diesel fuel injector was disposed downstream of the filter and a ceramic monolith of 400 cells per square inch (62 cells cm^{-2}) was coated with a $5\text{Cu} / \text{Beta-zeolite}$ catalyst of Example 1.

5 NO and NO_2 sensors were used to detect the amounts of these gases at various points in the exhaust system, and the amounts of detected NO_2 were used to calculate an amount of diesel fuel to be injected to obtain an $\text{HC}:\text{NO}_2$ ratio of 0.5 and 0.25 over the catalyst. (Since approximately 50% of NO_x downstream of the $\text{CRT}^{\text{®}}$ oxidation catalyst at up to about 400°C is NO_2 , these values correlate to an $\text{HC}:\text{NO}_x$ ratio of approximately 1.0 and 0.5 respectively). The
10 engine load was adjusted to increase temperature in the exhaust system and measurements were made after the system had been run at steady state conditions.

Figures 3 – 5 show the results for $\text{HC}:\text{NO}_2$ of 0.5. In the legends, the NO_2 decomposition catalyst is referred to as a "clean-up" catalyst. It can be seen that good NO_2 decomposition
15 activity is observed, although the % NO_2 decomposition does fall off at temperatures below about 300°C . A small amount of NO_x conversion of 7% peak at about 325°C is observed (results not shown). Under the conditions used, NO_2/NO_x is below 20% at every temperature except the lowest (250°C). The fall off in NO_2/NO_x ratio after the $\text{CRT}^{\text{®}}$ oxidation catalyst is due to the thermodynamic equilibrium favouring NO over NO_2 . Negligible HC slip was observed (results
20 not shown).

At $\text{HC}:\text{NO}_2$ of 0.25 (results shown in Figures 6 – 8), good NO_2 decomposition is still observed, but the conversion peaks at 80%. Again, a small amount of NO_x conversion (peak 6% at 325°C) was seen. Under the conditions used, NO_2/NO_x is below 20% at temperatures above
25 325°C . Negligible HC slip was observed.

CLAIMS:

1. A method of decomposing nitrogen dioxide (NO_2) in an exhaust gas of a lean-burn internal combustion engine, which method comprising adjusting the hydrocarbon : nitrogen oxides ($\text{HC}:\text{NO}_x$) ratio of the exhaust gas to from 0.1 to 2 and contacting this gas mixture with at least one support comprising at least one metal selected from the group consisting of rhodium, silver, iron and copper.
2. A method according to Claim 1, wherein the $\text{HC}:\text{NO}_2$ ratio is adjusted to from 0.05 to 1.
3. A method according to claim 1 or 2, wherein the step of adjusting the $\text{HC}:\text{NO}_x$ ratio is done at above 250°C .
4. A method according to claim 3, wherein the step of adjusting the $\text{HC}:\text{NO}_x$ ratio is done at up to 500°C .
5. A method according to claim 1, 2, 3 or 4, wherein the hydrocarbon is diesel fuel, gasoline fuel, natural gas (NG) or liquid petroleum gas (LPG).
6. An exhaust system for an internal combustion engine, which system comprising a catalyst for decomposing NO_2 with a suitable reductant, and means, in use, for adjusting the hydrocarbon : nitrogen oxides ($\text{HC}:\text{NO}_x$) ratio in an exhaust gas upstream of the catalyst to from 0.01 to 2, which catalyst comprising at least one support comprising at least one metal selected from the group consisting of rhodium, silver, iron and copper.
7. An exhaust system according to claim 6, wherein the means for adjusting is adapted to adjust the $\text{HC}:\text{NO}_2$ ratio of the exhaust gas to from 0.05 to 1.
8. An exhaust system according to claim 6 or 7, wherein the adjustment means is controlled, in use, to operate when the exhaust gas temperature is above 250°C .
9. An exhaust system according to claim 8, wherein the adjustment means is controlled, in use, to operate when the exhaust gas temperature is below 500°C .

10. An exhaust system according to claim 6, 7, 8 or 9, wherein the adjustment means comprises a control means comprising a processor.
- 5 11. An exhaust system according to claim 10, wherein the processor is part of an engine control unit (ECU).
- 10 12. An exhaust system according to claim 10 or 11, wherein the control means adjusts the HC:NO_x ratio in response to one or more of the following inputs: exhaust gas temperature; catalyst bed temperature; rate of exhaust gas mass flow; NO₂ in the exhaust gas; manifold vacuum; ignition timing; engine speed; throttle position; lambda value of the exhaust gas composition; quantity of fuel injected in the engine; position of an exhaust gas recirculation valve; and boost pressure.
- 15 13. An exhaust system according to claim 12, wherein the control means is operated according to stored look-up tables or an engine map in response to the at least one input.
- 20 14. An exhaust system according to any of claims 6 to 13, wherein the means for adjusting the HC:NO_x ratio comprises at least one of: means for injecting a reductant into the exhaust gas; means for adjusting the ignition timing of at least one engine cylinder; means for adjusting fuel injection timing of at least one engine cylinder; means for adjusting the engine air-to-fuel ratio; and adjustment of exhaust gas recirculation rate.
- 25 15. An exhaust system according to any of claims 6 to 14, wherein where the at least one metal is rhodium, the support is free of other platinum group metals (PGMs).
16. An exhaust system according to any of claims 6 to 15, wherein the NO₂ decomposition catalyst is disposed downstream of an oxidation catalyst comprising at least one PGM, preferably at least one of platinum and palladium.
- 30 17. An exhaust system according to claim 16, wherein the oxidation catalyst is on a diesel particulate filter.
18. An exhaust system according to claim 17, wherein the oxidation catalyst is associated with a NO_x absorbent material.

19. An exhaust system according to claim 16, 17 or 18, wherein the NO₂ decomposition catalyst is disposed on a downstream end of a filter.
- 5 20. An exhaust system according to any of claims 6 to 20, wherein the filter is a wall-flow filter.
- 10 21. An exhaust system according to any of claims 14 to 20, when appendant to claim 14 wherein the reductant injecting means introduces the reductant into the exhaust system upstream of the NO₂ decomposition catalyst and downstream of any PGM oxidation catalyst.
- 15 22. An exhaust system according to any of claims 6 to 21, wherein the at least one support comprises from 0.1 to 5.0 wt% rhodium based on the total weight of the at least one support.
- 20 23. An exhaust system according to claim 22, wherein the at least one support comprises from 0.25 to 2.5 wt% rhodium based on the total weight of the at least one support.
- 25 24. An exhaust system according to any of claims 6 to 21, wherein the at least one support comprises from 0.1 to 5.0 wt% silver based on the total weight of the at least one support.
26. An exhaust system according to claim 24, wherein the at least one support comprises from 0.25 to 2.5 wt% silver based on the total weight of the at least one support.
27. An exhaust system according to any of claims 6 to 21, wherein the at least one support comprises from 1 to 10 wt% copper based on the total weight of the support.
- 30 28. An exhaust system according to claim 26, wherein the at least one support comprises from 2.5 to 7.5 wt% copper based on the total weight of the at least one support.
29. An exhaust system according to any of claims 6 to 21, wherein the at least one support comprises from 1 to 10 wt% iron based on the total weight of the at least one support.

29. An exhaust system according to claim 28, wherein the at least one support comprises from 2.5 to 7.5 wt% iron based on the total weight of the at least one support.
30. An exhaust system according to any of claims 6 to 29, wherein the at least one support
5 comprises alumina, ceria, zirconia, titania, silica, chromia, a zeolite or a mixture, composite oxide or mixed oxide of any two or more thereof.
31. An exhaust system according to claim 30, wherein the composite oxide or mixed oxide
10 comprises silica-alumina, a silica-zirconia, alumina-zirconia, alumina-chromia, alumina-ceria, ceria-titania or ceria-zirconia.
32. An exhaust system according to claim 31, wherein the zeolite is ZSM-5, β -zeolite, Y-zeolite or mordenite.
- 15 33. An exhaust system according to any of the claims 6 to 32, wherein the at least one support and/or the particulate oxide material is doped with at least one of lanthanum, barium, cerium, tungsten, silica and manganese.
34. An exhaust system according to any of claims 6 to 33, wherein the catalyst comprises 5
20 wt% copper and the at least one support is zeolite ZSM-5 and/or β -zeolite.
35. An exhaust system according to any of claims 6 to 34, wherein the catalyst comprises 5 wt% iron and the at least one support is zeolite ZSM-5 and/or β -zeolite.
- 25 36. An exhaust system according to any of claims 6 to 35, wherein the catalyst comprises 2 wt% silver supported on alumina.
37. An exhaust system according to any of claims 6 to 36, wherein the catalyst comprises 0.5
30 wt% rhodium supported on alumina.
38. An internal combustion engine comprising an exhaust system according to any of claims 6 to 37.

39. An engine according to claim 38 fuelled with diesel fuel, gasoline fuel, natural gas (NG) or liquid petroleum gas (LPG).

40. A vehicle, such as a mining vehicle, comprising an engine according to claim 38 or 39.

5

41. A method of decomposing nitrogen dioxide (NO_2) substantially as described herein.

42. An exhaust system substantially as described herein.

10 43. An internal combustion engine substantially as described herein.

ABSTRACT

5

METHOD OF DECOMPOSING NITROGEN DIOXIDE

10 A method of decomposing nitrogen dioxide in an exhaust gas of a lean-burn internal combustion engine comprises adjusting the hydrocarbon : nitrogen oxides (HC:NO_x) ratio of the exhaust gas to from 0.1 to 2 and contacting this exhaust gas mixture with at least one support comprising at least one metal selected from the group consisting of rhodium, silver, iron and copper.

[Figure 1]

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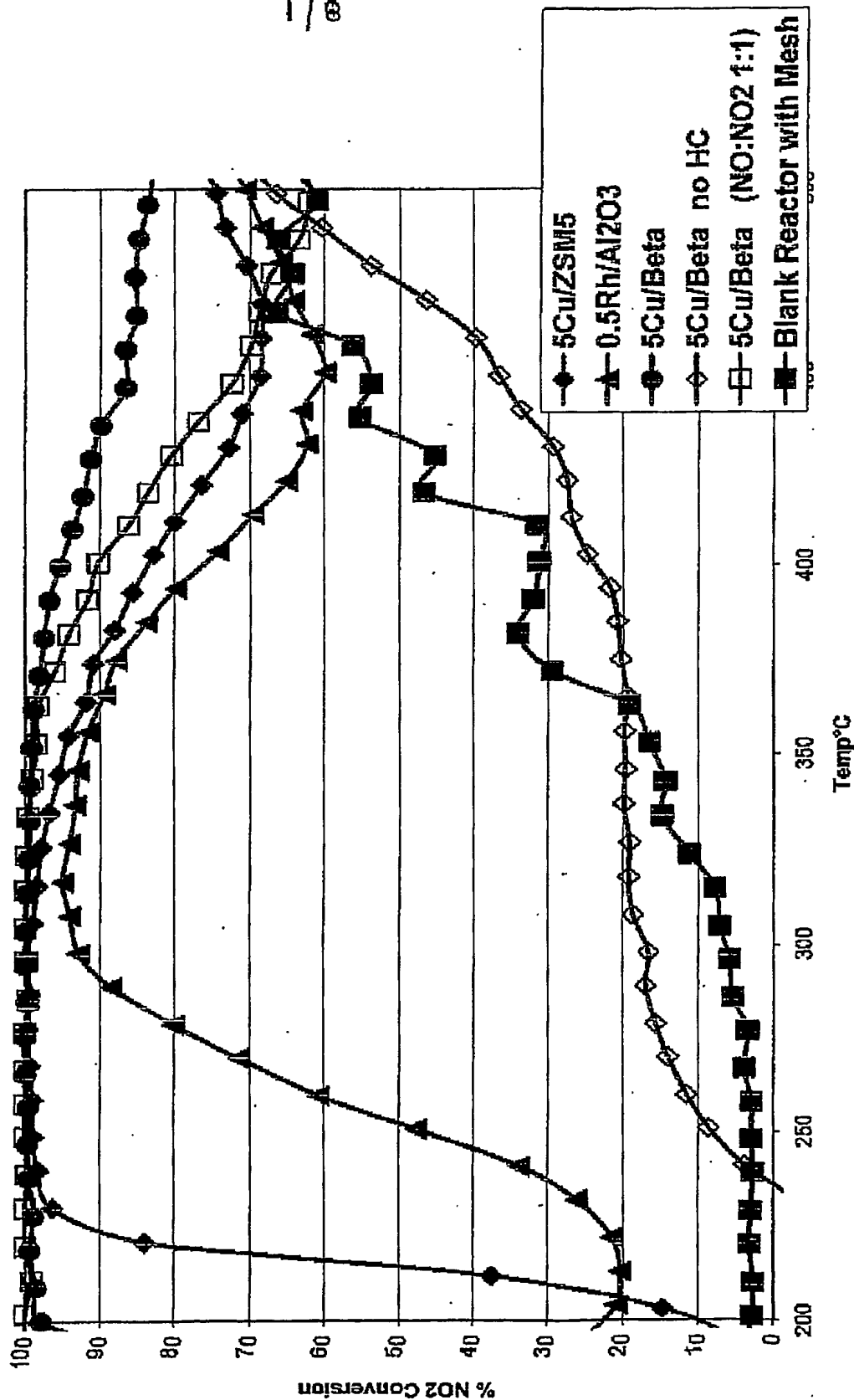
Effect of Diesel Fuel (120ppm C4) on NO₂ Decomposition

Fig 1.

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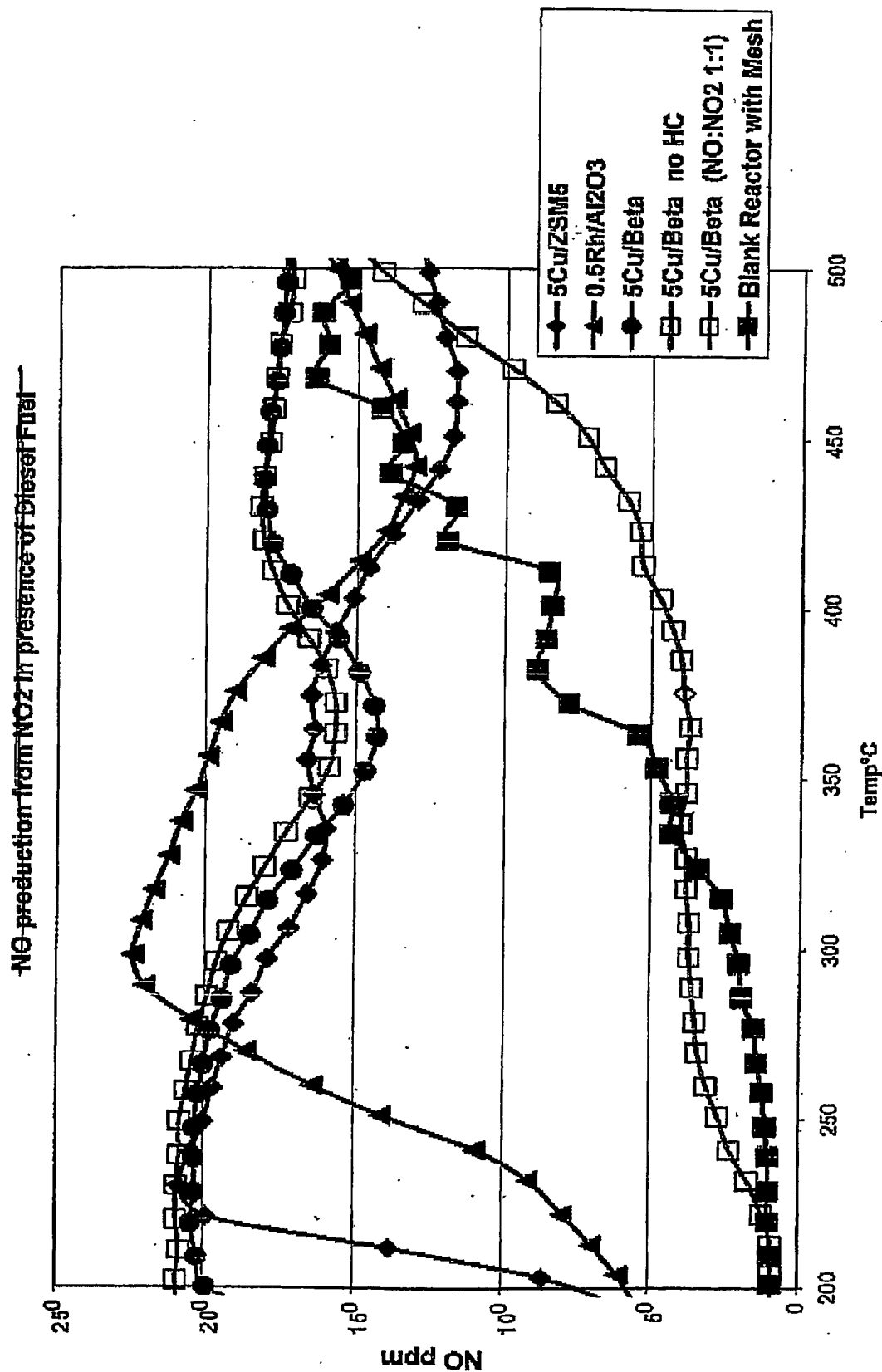


Fig 2.

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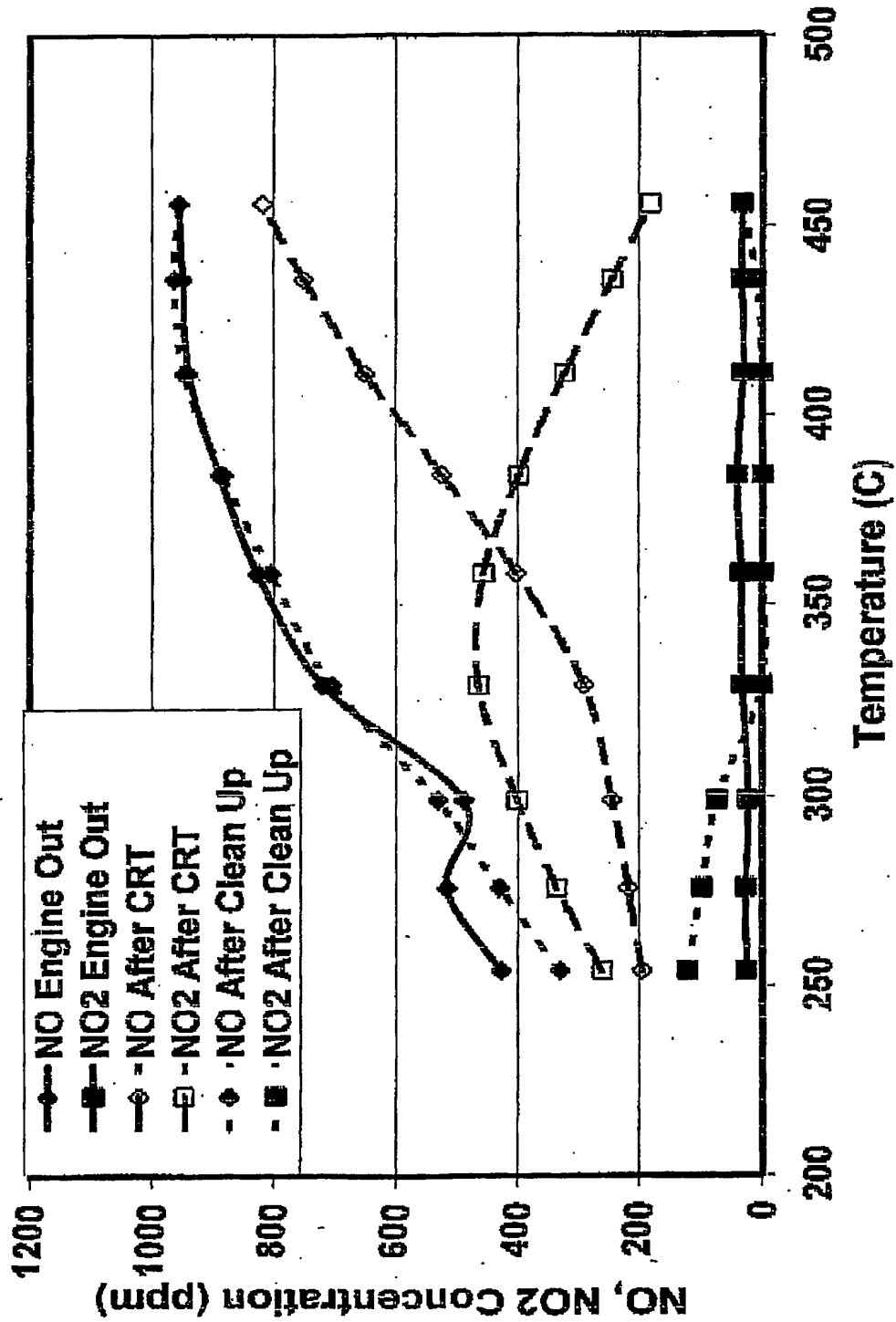


Fig 3.

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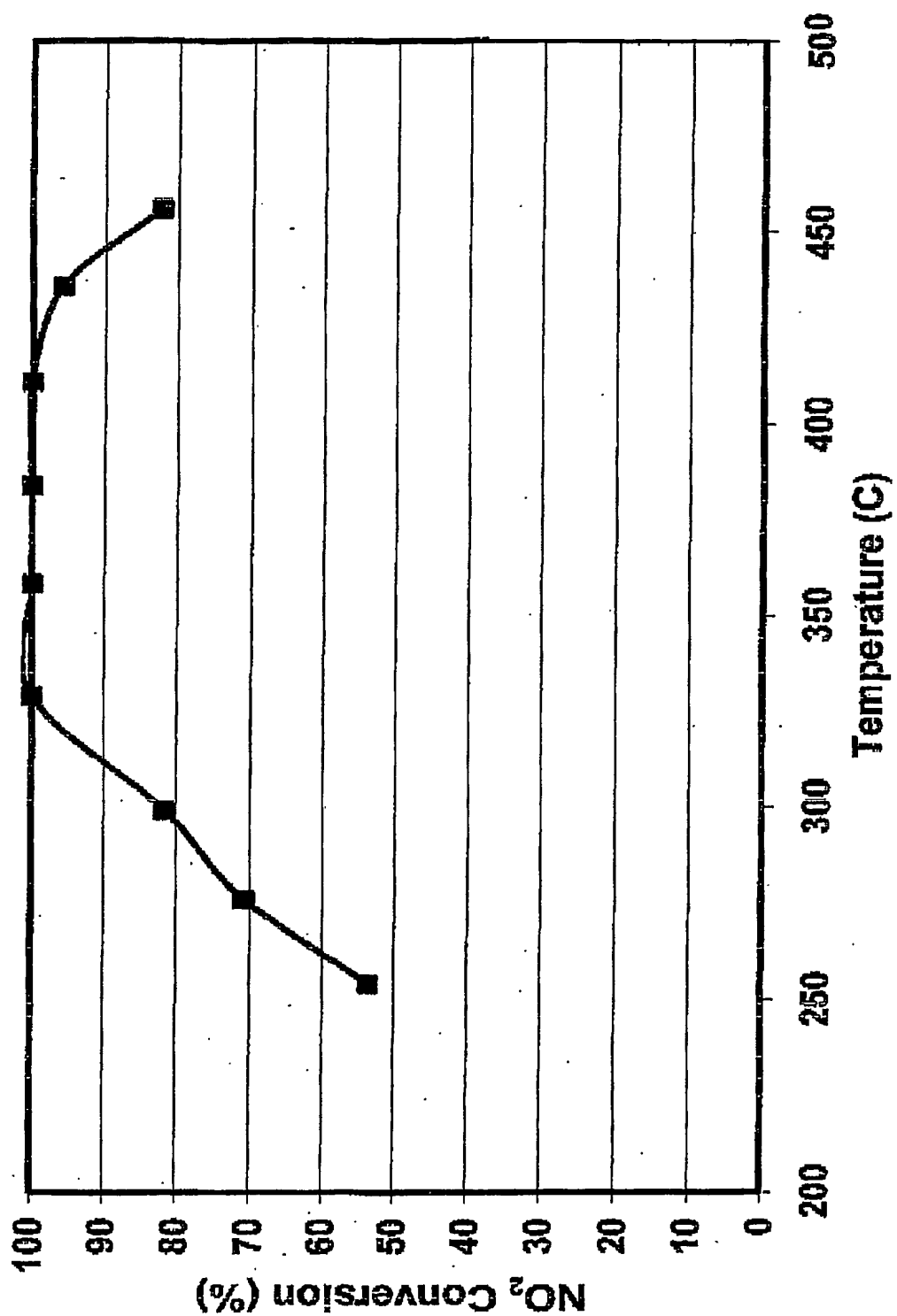


Fig 4.

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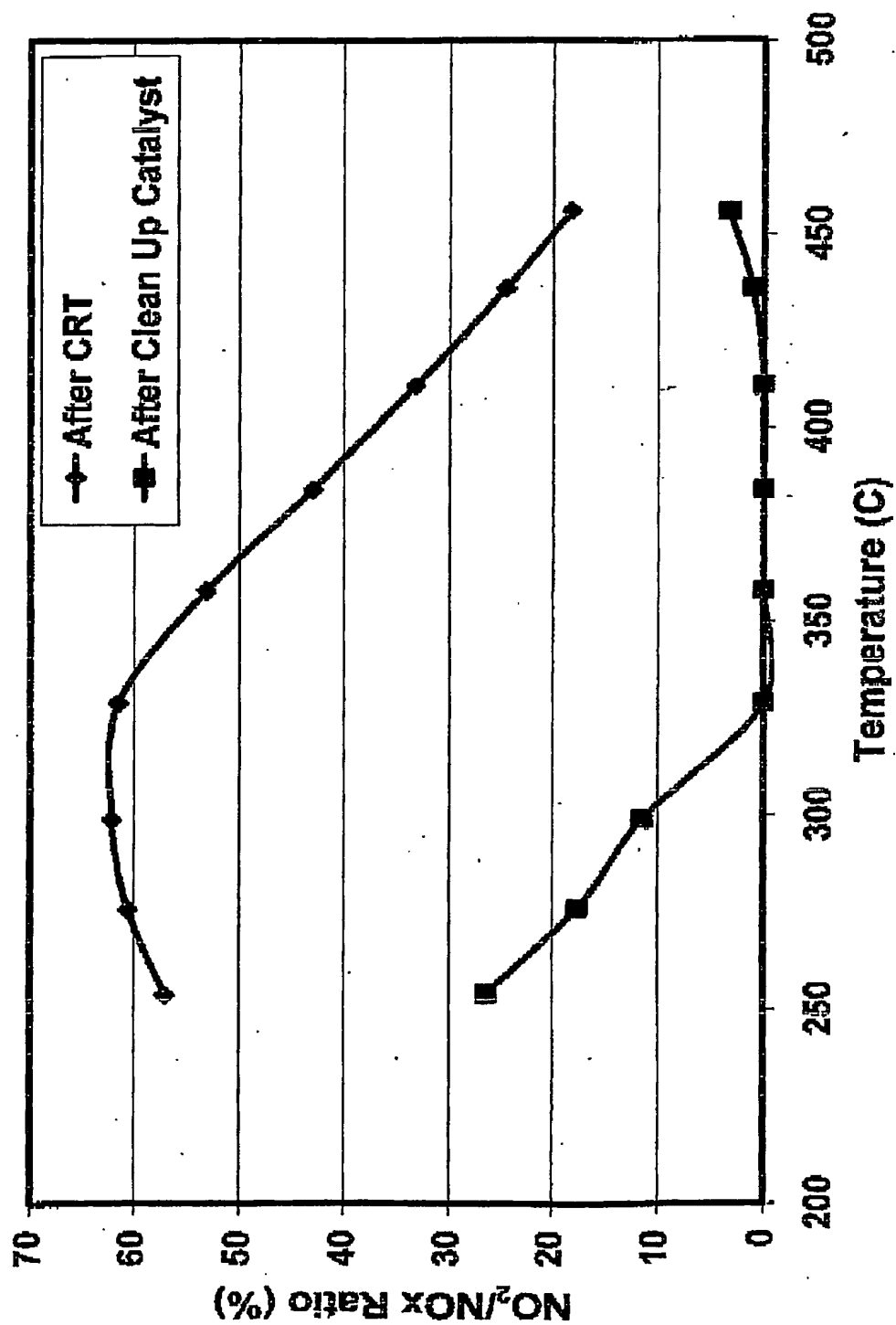


FIG. 5

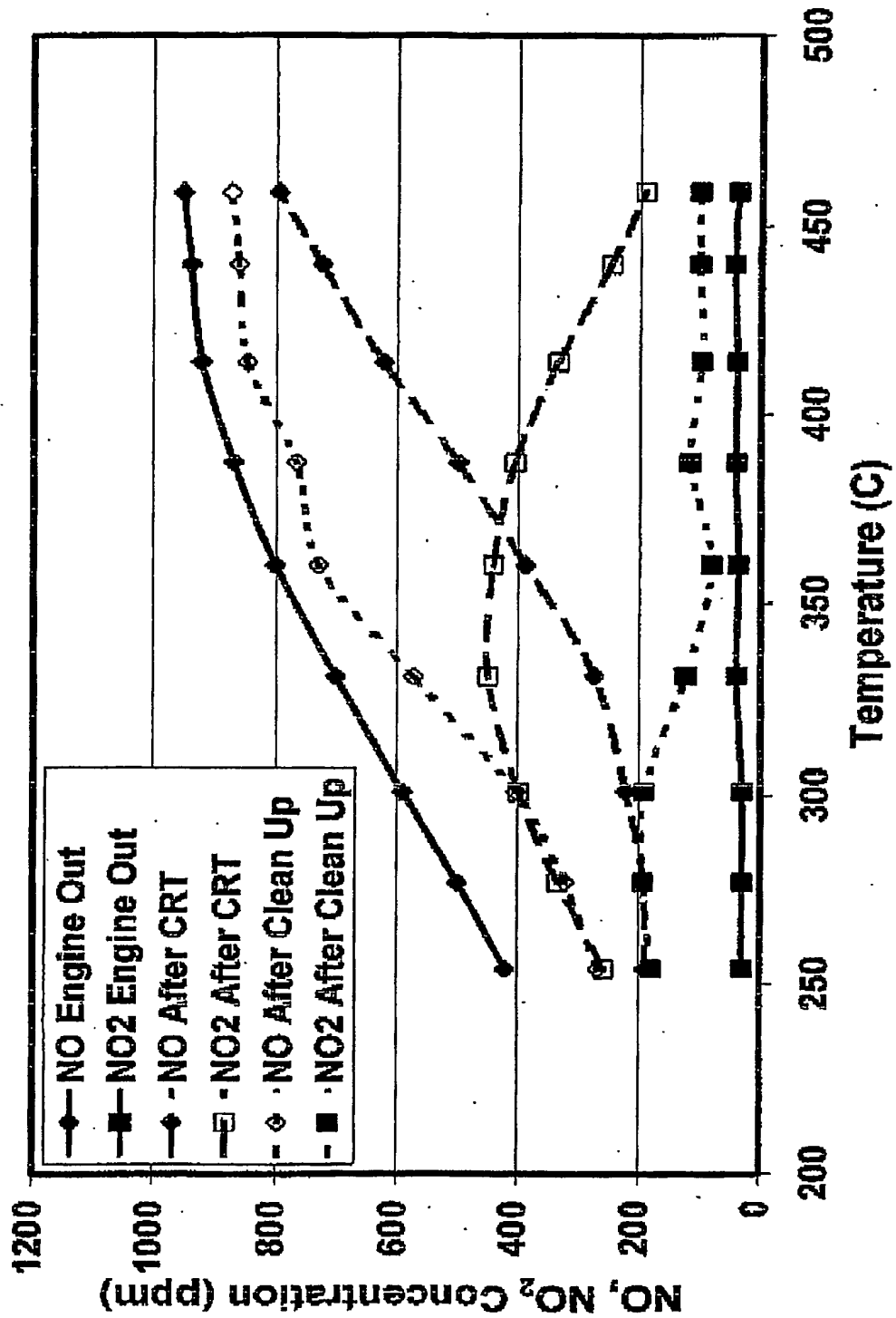


FIG 6.

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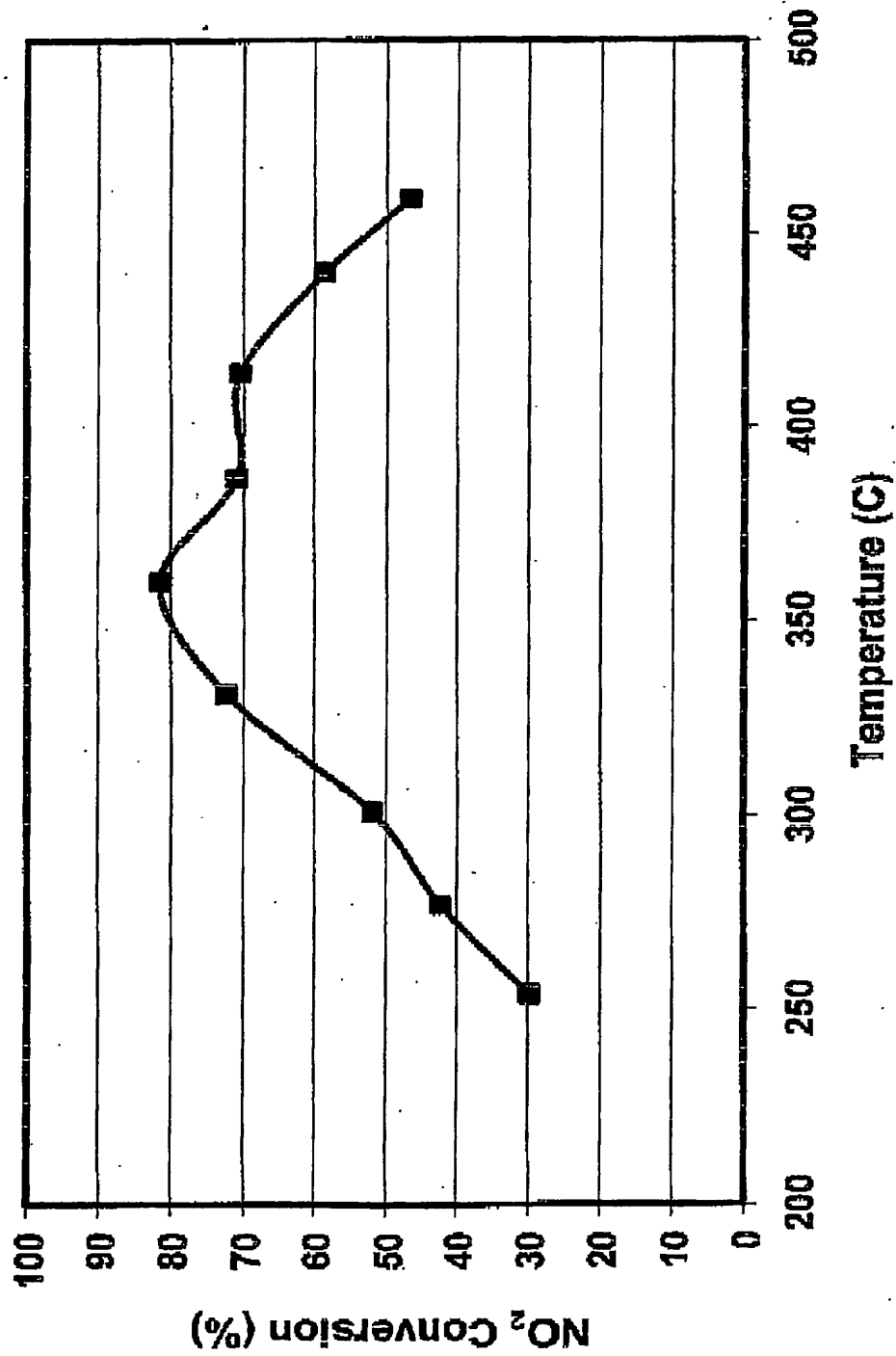


FIG 7.

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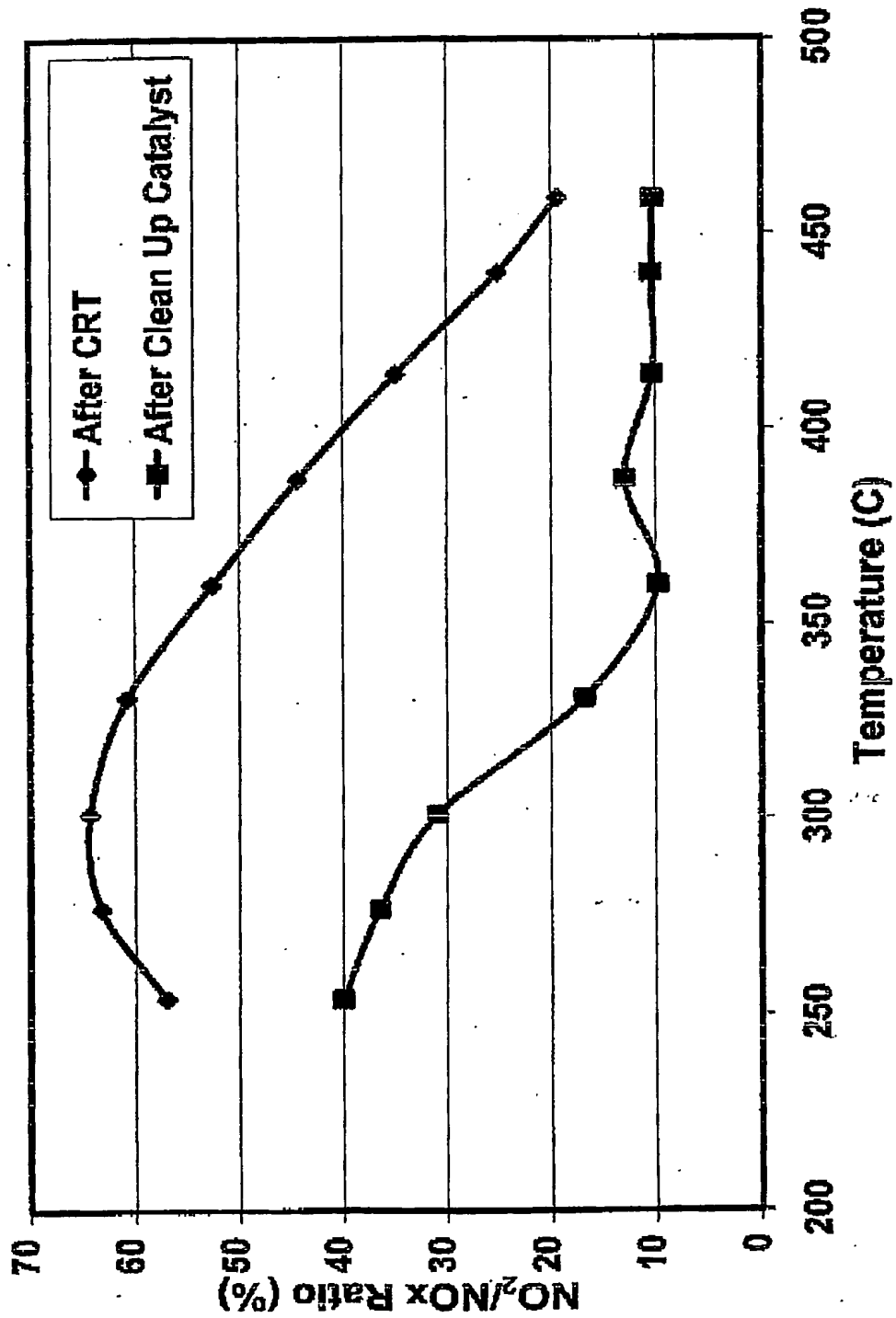


Fig 8.

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